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(54) Title: ZEOLITE Me-UTD-1		
(57) Abstract		
<p>An aluminosilicate zeolite is disclosed which has a silica/alumina mole ratio of about 500 or less and pores with at least one cross-sectional dimension greater than 7.5 Angstroms. Also disclosed is a zeolite comprising a first oxide selected from the group consisting of silicon oxide, germanium oxide and mixtures thereof and a second oxide selected from the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, the zeolite having, after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to the second oxide of about 500 or less. The zeolites are useful in catalysts for hydrocarbon conversion reactions.</p>		

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01 ZEOLITE Me-UTD-1

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04 BACKGROUND OF THE INVENTION

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Field of the Invention

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The present invention relates to new crystalline zeolite Me-UTD-1, methods
07 for preparing Me-UTD-1, and processes employing a catalyst comprising Me-UTD-1.

08

State of the Art

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Because of their unique sieving characteristics, as well as their catalytic
10 properties, crystalline molecular sieves and zeolites are especially useful in applications
11 such as hydrocarbon conversion, gas drying and separation. Although many different
12 crystalline molecular sieves have been disclosed, there is a continuing need for new
13 zeolites with desirable properties for gas separation and drying, hydrocarbon and
14 chemical conversions, and other applications. New zeolites may contain novel internal
15 pore architectures, providing enhanced selectivities in these processes.

16

Crystalline aluminosilicates are usually prepared from aqueous reaction
17 mixtures containing alkali or alkaline earth metal oxides, silica, and alumina.

18

Crystalline borosilicates are usually prepared under similar reaction conditions except
19 that boron is used in place of aluminum. By varying the synthesis conditions and the
20 composition of the reaction mixture, different zeolites can often be formed.

21

U.S. Patent No. 5,489,424, issued February 6, 1996 to Balkus et al., discloses
22 an all-silica zeolite designated "UTD-1" which is prepared using a
23 bis(pentamethylcyclopentadienyl) cobalt (III) ion as a templating agent. Balkus et al.
24 characterize UTD-1 as having a pore size at least as large as 7 Å. In addition, the X-
25 ray diffraction pattern for as-synthesized UTD-1 is provided.

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SUMMARY OF THE INVENTION

32 The present invention is directed to a family of crystalline molecular sieves with
33 unique properties, referred to herein as "zeolite Me-UTD-1" or simply "Me-UTD-1".

34

The designation "Me-UTD-1" is used to indicate that the zeolite has the crystal
structure of the UTD-1 disclosed in U.S. Patent No. 5,489,424, but contains atoms
other than silicon and oxygen, preferably a metal ("Me") such as aluminum, in the

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01 crystal framework. Preferably Me-UTD-1 is obtained in its aluminosilicate form. As
02 used herein the term "aluminosilicate" refers to a zeolite containing oxides of both
03 aluminum and silicon in the framework.

04 In accordance with the present invention, there is provided an aluminosilicate
05 zeolite having a silica/alumina mole ratio of about 500 or less and having pores with at
06 least one cross-sectional dimension greater than 7.5 Angstroms, preferably at least
07 about 8 Angstroms. The calcined zeolite has the X-ray diffraction lines of Table I.

08 Further in accordance with this invention there is provided a zeolite comprising
09 a first oxide selected from the group consisting of silicon oxide, germanium oxide and
10 mixtures thereof and a second oxide selected from the group consisting of aluminum
11 oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron
12 oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,
13 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and having a
14 mole ratio of the first oxide to the second oxide of about 500 or less. The present
15 invention also includes this zeolite which is predominantly in the hydrogen form, which
16 hydrogen form is prepared by ion exchanging with an acid or with a solution of an
17 ammonium salt followed by a second calcination. Further provided is this zeolite made
18 substantially free of acidity by neutralizing said zeolite with a basic metal.

19 Also provided in accordance with the present invention is a method of preparing a
20 boron-containing zeolite comprising oxides of born and silica, said zeolite having, after
21 calcination, the X-ray diffraction lines of Table I, said method comprising:

22 (a) preparing an aqueous solution containing calcined boron-containing
23 Beta zeolite, an alkali metal or alkaline earth metal cation, and a
24 bis(pentamethylcyclopentadienyl) cobalt (III) ion having an anionic counterion which is
25 not detrimental to the formation of the boron-containing zeolite;

26 (b) maintaining the aqueous solution under conditions sufficient to form
27 crystals of the boron-containing zeolite; and

28 (c) recovering crystals of the boron-containing zeolite.

29 The present invention additionally provides a process for converting
30 hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon

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01 converting conditions with a catalyst comprising the Me-UTD-1 zeolite of this
02 invention, preferably predominantly in the hydrogen form.

03 Further provided by the present invention is a hydrocracking process
04 comprising contacting a hydrocarbon feedstock under hydrocracking conditions with a
05 catalyst comprising the Me-UTD-1 of this invention, preferably predominantly in the
06 hydrogen form.

07 This invention also includes a dewaxing process comprising contacting a
08 hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the
09 Me-UTD-1 of this invention, preferably predominantly in the hydrogen form.

10 This invention also includes a process for improving the viscosity index of the
11 dewaxed product of waxy hydrocarbon feeds comprising contacting the waxy
12 hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising
13 the Me-UTD-1 of this invention, preferably predominantly in the hydrogen form.

14 Also provided by this invention is a process for producing a C₂₀₊ lube oil from a
15 C₂₀₊ olefin feed comprising isomerizing said olefin feed over a catalyst comprising at
16 least one Group VIII metal and the Me-UTD-1 of this invention, preferably
17 predominantly in the hydrogen form.

18 Further provided in accordance with the present invention is a process for
19 catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F and
20 containing straight chain and slightly branched chain hydrocarbons comprising
21 contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas at a
22 hydrogen pressure of about 15-3000 psi with a catalyst comprising at least one Group
23 VIII metal and the Me-UTD-1 of this invention, preferably predominantly in the
24 hydrogen form. Also provided is such a process wherein said catalyst comprises a
25 layered catalyst comprising a first layer comprising at least one Group VIII metal and
26 the Me-UTD-1 of this invention, and a second layer comprising an aluminosilicate
27 zeolite which is more shape selective than the zeolite of said first layer.

28 The present invention also provides a process for preparing a lubricating oil
29 which comprises:

30 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an
31 effluent comprising a hydrocracked oil, and catalytically dewaxing said effluent

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01 comprising hydrocracked oil at a temperature of at least about 400°F and at a pressure
02 of from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a
03 catalyst comprising at least one Group VIII metal and the Me-UTD-1 of this invention,
04 preferably predominantly in the hydrogen form.
05

06 Further provided is a process for isomerization dewaxing a raffinate comprising
07 contacting said raffinate in the presence of added hydrogen with a catalyst comprising
08 at least one Group VIII metal and the Me-UTD-1 of this invention, preferably
09 predominantly in the hydrogen form.

10 Also included in this invention is a process for increasing the octane of a
11 hydrocarbon feedstock to produce a product having an increased aromatics content
12 comprising contacting a hydrocarbonaceous feedstock which comprises normal and
13 slightly branched hydrocarbons having a boiling range above about 40°C and less than
14 about 200°C, under aromatic conversion conditions with a catalyst comprising the Me-
15 UTD-1 of this invention, preferably made substantially free of acidity by neutralizing
16 said zeolite with a basic metal. Also provided in this invention is such a process
17 wherein the zeolite contains a Group VIII metal component.
18

20 Also provided by the present invention is a catalytic cracking process
21 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic
22 cracking conditions in the absence of added hydrogen with a catalyst comprising the
23 Me-UTD-1 of this invention, preferably predominantly in the hydrogen form. Also
24 included in this invention is such a catalytic cracking process wherein the catalyst
25 additionally comprises a large pore crystalline cracking component.
26

27 The present invention further provides an isomerizing process for isomerizing
28 C₄ to C₇ hydrocarbons, comprising contacting a catalyst, comprising at least one
29 Group VIII metal impregnated on the Me-UTD-1 of this invention, preferably
30 predominantly in the hydrogen form, with a feed having normal and slightly branched
31 C₄ to C₇ hydrocarbons under isomerizing conditions. Also provided is such an
32 isomerization process wherein the catalyst has been calcined in a steam/air mixture at
33 an elevated temperature after impregnation of the Group VIII metal, preferably
34 platinum.

01 This invention also provides a process for alkylating an aromatic hydrocarbon
02 which comprises contacting under alkylation conditions at least a mole excess of an
03 aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid phase
04 conditions and in the presence of a catalyst comprising the Me-UTD-1 of this
05 invention, preferably predominantly in the hydrogen form.

06 This invention additionally provides a process for transalkylating an aromatic
07 hydrocarbon which comprises contacting under transalkylating conditions an aromatic
08 hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid phase
09 conditions and in the presence of a catalyst comprising the Me-UTD-1 of this
10 invention, preferably predominantly in the hydrogen form.

11 Further provided by this invention is a process to convert paraffins to aromatics
12 which comprises contacting paraffins with a catalyst comprising gallium, zinc or a
13 compound of gallium or zinc and the Me-UTD-1 of this invention, preferably made
14 substantially free of acidity.

15 Also provided is a process for isomerizing olefins comprising contacting said
16 olefin under conditions which cause isomerization of the olefin with a catalyst
17 comprising the Me-UTD-1 of this invention, preferably predominantly in the hydrogen
18 form.

19 Further provided in accordance with this invention is a process for isomerizing
20 an isomerization feed comprising an aromatic C₈ stream of xylene isomers or mixtures
21 of xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-,
22 meta and para xylenes is obtained, said process comprising contacting said feed under
23 isomerization conditions with a catalyst comprising the Me-UTD-1 of this invention,
24 preferably predominantly in the hydrogen form.

25 The present invention further provides a process for oligomerizing olefins
26 comprising contacting an olefin feed under oligomerization conditions with a catalyst
27 comprising the Me-UTD-1 of this invention, preferably predominantly in the hydrogen
28 form.

29 This invention also provides a process for converting lower alcohols and other
30 oxygenated hydrocarbons comprising contacting said lower alcohol or other
31 oxygenated hydrocarbon with a catalyst comprising the Me-UTD-1 of this invention,

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01 preferably predominantly in the hydrogen form, under conditions to produce liquid
02 products.

03 Also provided by the present invention is an improved process for the reduction
04 of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said
05 process comprises contacting the gas stream with a zeolite, the improvement
06 comprising using as the zeolite, the Me-UTD-1 of this invention. The zeolite may
07 contain a metal or metal ions capable of catalyzing the reduction of the oxides of
08 nitrogen, and the process may be conducted in the presence of a stoichiometric excess
09 of oxygen. In a preferred embodiment, the gas stream is the exhaust stream of an
10 internal combustion engine.

11 This invention also provides a process for converting hydrocarbons comprising
12 contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a
13 catalyst comprising a Group VIII metal and a silica zeolite having, after calcination, the
14 X-ray diffraction lines of Table IA.

15 DETAILED DESCRIPTION OF THE INVENTION

16 The present invention comprises a family of crystalline, large pore zeolites,
17 designated "Me-UTD-1". The Me-UTD-1 zeolites have pores which have at least one
18 cross-sectional dimension which is at least 7.5 Angstroms, preferably at least about 8
19 Angstroms, more preferably about 8 to about 10 Angstroms. The pores appear to be
20 in the form of 14 member rings.

21 In preparing Me-UTD-1 zeolites, a bis(pentamethylcyclopentadienyl) cobalt
22 (III) ion is used as a crystallization template. In general, Me-UTD-1 is prepared by
23 contacting an active source of silicon oxide and boron oxide (boron-containing Beta
24 zeolite in its calcined form can be used as the sources of both the silicon oxide and
25 boron oxide) with the bis(pentamethylcyclopentadienyl) cobalt (III) ion templating
26 agent (designated as "Q" below) to form the borosilicate form of UTD-1 ("B-UTD-
27 1"), followed by substitution of the boron in the B-UTD-1 framework with metal
28 atoms, preferably aluminum.

29 The B-UTD-1 is prepared from a reaction mixture having the composition
30 shown in Table A below.

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01	<u>TABLE A</u>		
02	<u>Reaction Mixture</u>		
03		General	Preferred
04	Z/Y	0.01 - 0.10	0.06 - 0.08
05	OH ⁻ /YO ₂	0.10 - 0.30	0.18 - 0.25
06	Q/YO ₂	0.05 - 0.30	0.08 - 0.15
07	M _{2x} /YO ₂	0.05 - 0.20	0.08 - 0.12
08	H ₂ O/YO ₂	20 - 100	30 - 60
09			
10			
11			
12	where Y is selected from the group consisting of silicon, germanium and mixtures		
13	thereof; Z represents boron; Q comprises a bis(pentamethylcyclopentadienyl) cobalt		
14	(III) ion; M is an alkali or alkaline earth metal cation; and x is the valence of M.		
15	The preferred source of silicon oxide and boron oxide is calcined boron-		
16	containing zeolite Beta ("B-Beta"). One advantage of using B-Beta is that it provides		
17	B-UTD-1 with very small crystallite size, typically about 2000 Å or less, preferably		
18	about 500-1000 Å along the C axis as estimated by TEM.		
19			
20	In practice, B-UTD-1 is prepared by a process comprising:		
21	(a) preparing an aqueous solution containing calcined B-Beta, an alkali		
22	metal or alkaline earth metal cation, and a		
23	bis(pentamethylcyclopentadienyl) cobalt (III) ion having an anionic		
24	counterion which is not detrimental to the formation of B-UTD-1;		
25	(b) maintaining the aqueous solution under conditions sufficient to		
26	form crystals of B-UTD-1; and		
27	(c) recovering the crystals of B-UTD-1.		
28			
29	Typically, an alkali metal hydroxide and/or an alkaline earth metal hydroxide,		
30	such as the hydroxide of sodium, potassium, lithium, cesium, rubidium, calcium, and		
31	magnesium, is used in the reaction mixture; however, this component can be omitted		
32	so long as the equivalent basicity is maintained. The templating agent may be used to		
33	provide hydroxide ion. Thus, it may be beneficial to ion exchange, for example, the		
34	halide for hydroxide ion, thereby reducing or eliminating the alkali metal hydroxide		
	quantity required. The alkali metal cation or alkaline earth cation may be part of the		

30 Typically, an alkali metal hydroxide and/or an alkaline earth metal hydroxide,
 31 such as the hydroxide of sodium, potassium, lithium, cesium, rubidium, calcium, and
 32 magnesium, is used in the reaction mixture; however, this component can be omitted
 33 so long as the equivalent basicity is maintained. The templating agent may be used to
 34 provide hydroxide ion. Thus, it may be beneficial to ion exchange, for example, the
 halide for hydroxide ion, thereby reducing or eliminating the alkali metal hydroxide
 quantity required. The alkali metal cation or alkaline earth cation may be part of the

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01 as-synthesized crystalline oxide material, in order to balance valence electron charges
02 therein.

The reaction mixture is maintained at an elevated temperature until the crystals of the B-UTD-1 zeolite are formed. The hydrothermal crystallization is usually conducted under autogenous pressure, at a temperature between about 140°C and 170°C. The crystallization period is typically greater than 1 day and preferably from about 3 days to about 20 days.

09 The zeolite may be prepared with or without mild stirring or agitation.

During the hydrothermal crystallization step, the B-UTD-1 crystals can be allowed to nucleate spontaneously from the reaction mixture. The use of B-UTD-1 crystals as seed material can be advantageous in decreasing the time necessary for complete crystallization to occur. In addition, seeding can lead to an increased purity of the product obtained by promoting the nucleation and/or formation of B-UTD-1 over any undesired phases. When used as seeds, B-UTD-1 crystals are added in an amount between 0.1 and 10% of the weight of silica used in the reaction mixture.

Once the zeolite crystals have formed, the solid product is separated from the reaction mixture by standard mechanical separation techniques such as filtration. The crystals are water-washed and then dried, e.g., at 90°C to 150°C for from 8 to 24 hours, to obtain the as-synthesized B-UTD-1 zeolite crystals, which, at this point, still contain some of the bis(pentamethylcyclopentadienyl) cobalt (III) ion template. The drying step can be performed at atmospheric pressure or under vacuum.

B-UTD-I further has a composition, as synthesized and in the anhydrous state, in terms of mole ratios, shown in Table B below.

TABLE B

As-Synthesized B-UTD-1

30	YO_2/Z	about 50 or greater
31	M_{2x}/YO_2	≤ 0.05
33	Q/YO_2	0.01-0.03

34 where Y, Z, M, x and Q are as defined above.

The B-UTD-1 can then be treated to remove the cobalt-containing template and to exchange the boron in the B-UTD-1 framework with another element, e.g.,

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01 aluminum. This is typically accomplished in two sequential steps. First, the boron can
02 be removed from the framework of the B-UTD-1 by treatment with an excess of
03 protons at pH preferably below 2. A variety of acids, such as HCl, HNO₃ or H₂SO₄,
04 can be used. Components which buffer the system above about pH 3 will slow down
05 the process. It is helpful to heat these acidic solutions, usually for 1-3 days of reaction
06 to ensure a greater than 90% removal of the boron.

08 Thus, the B-UTD-1 is typically refluxed in acid, such as 2N HCl until the
09 cobalt is dissolved. (The solution will turn pink as the cobalt dissolves.) This acid
10 treatment also removes the boron from the B-UTD-1. When the acid treatment is
11 finished, the zeolite crystals can be recovered, washed and reheated to about 140°C in
12 a solution containing a salt of the desired boron-replacing cation or cations. Thus, the
13 Me-UTD-1 of this invention contains substantially no cobalt, and has at least part of
14 the boron replaced by another cation or cations.

16 After the cobalt has been removed from the B-UTD-1 and the boron has been
17 replaced by another element, the resulting Me-UTD-1 has a mole ratio of a first oxide
18 selected from the group consisting of silicon oxide, germanium oxide and mixtures
19 thereof to a second oxide selected from the group consisting of aluminum oxide,
20 gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,
21 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide of about
22 500 or less, preferably about 500 to about 50, more preferably about 200 to about 50.

25 Me-UTD-1 is comprised of a framework structure or topology which is
26 characterized by its X-ray diffraction pattern. Me-UTD-1 zeolites, in the calcined
27 form, have a crystalline structure whose X-ray powder diffraction pattern exhibit the
28 characteristic lines shown in Table I.

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TABLE I
Calcined Me-UTD-1

	2 Theta	d	Relative Intensity ^(a)
6.0 ± 0.1	14.4-15.0	VS	
7.6 ± 0.1	11.5-11.8	S	
14.55 ± 0.15	6.0-6.1	W-M	
19.8 ± 0.1	4.4-4.5	M	
21.2 ± 0.1	4.17-4.21	VS	
22.0 ± 0.1	4.01-4.06	M	
22.5 ± 0.1	3.92-3.96	M	
24.5 ± 0.05	3.64-3.68	W	

^(a) The X-ray patterns provided are based on a relative intensity scale in which the strongest line in the X-ray pattern is assigned a value of 100: W(weak) is less than 10; M(medium) is between 10 and 40; S(strong) is between 40 and 60; VS(very strong) is greater than 60.

22 The X-ray powder diffraction pattern for B-UTD-1 also exhibits the characteristic lines
23 shown in Table I.

24 All-silica UTD-1 zeolite (such as that disclosed in U.S. Patent No. 5,489,424),
25 in the calcined form, has a crystalline structure whose X-ray powder diffraction pattern
26 exhibit the characteristic lines shown in Table IA below.
27

TABLE IA
Calcined all-silica UTD-1

	2 Theta	d	Relative Intensity
30			
31			
32	6.00 ± 0.05	14.6-14.9	VS
33	7.60 ± 0.10	11.5-11.8	S-VS
34	14.5 ± 0.10	6.05-6.15	W-M
	18.0 ± 0.10	4.89-4.95	W-M
	19.7 ± 0.10	4.48-4.53	W-M

2 Theta	d	Relative Intensity
21.0 ± 0.10	4.21-4.25	M-S
24.2 ± 0.10	3.66-3.69	W-M
24.95 ± 0.10	3.55-3.58	W-M

1
2 The X-ray powder diffraction patterns were determined by standard techniques.
3 The radiation was the K-alpha/doublet of copper. The peak heights and the positions,
4 as a function of 2θ where θ is the Bragg angle, were read from the relative intensities
5 of the peaks, and d, the interplanar spacing in Angstroms corresponding to the
6 recorded lines, can be calculated.

7 Unless otherwise indicated, the variation in the scattering angle (two theta)
8 measurements, due to instrument error and to differences between individual samples,
9 is estimated at +/- 0.20 degrees.

10 Representative peaks from the X-ray diffraction pattern of calcined Me-UTD-1
11 are shown in Table I. Calcination can also result in changes in the intensities of the
12 peaks as compared to patterns of the "as-made" material, as well as minor shifts in the
13 diffraction pattern. The zeolite produced by exchanging the metal or other cations
14 present in the zeolite with various other cations (such as H⁺ or NH₄⁺) yields essentially
15 the same diffraction pattern, although again, there may be minor shifts in the
16 interplanar spacing and variations in the relative intensities of the peaks. Minor
17 variations in the diffraction pattern can result from variations in the silica-to-alumina
18 (or other oxide) mole ratio of the particular sample due to changes in lattice constants.
19 In addition, sufficiently small crystals will affect the shape and intensity of peaks,
20 leading to significant peak broadening. Notwithstanding these minor perturbations, the
21 basic crystal lattice remains unchanged by these treatments.

22 Crystalline Me-UTD-1 normally will be thermally treated (calcined). Usually, it
23 is desirable to remove the alkali metal cation by ion exchange and replace it with
24 hydrogen, ammonium, or any desired metal ion. The zeolite can be leached with
25 chelating agents, e.g., EDTA or dilute acid solutions, to increase the silica to alumina
26 (or other oxide) mole ratio. The zeolite can also be steamed; steaming helps stabilize
27 the crystalline lattice to attack from acids.

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01 The zeolite can be used in intimate combination with hydrogenating
02 components, such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt,
03 chromium, manganese, or a noble metal, such as palladium or platinum, for those
04 applications in which a hydrogenation-dehydrogenation function is desired.
05

06 Metals may also be introduced into the zeolite by replacing some of the cations
07 in the zeolite with metal cations via ion exchange techniques. Typical replacing cations
08 can include metal cations, e.g., rare earth, Group IA, Group IIA and Group VIII
09 metals, as well as their mixtures. Of the replacing metallic cations, cations of metals
10 such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are
11 particularly preferred.
12

13 The hydrogen, ammonium, and metal components can be ion-exchanged into
14 the Me-UTD-1. The zeolite can also be impregnated with the metals, or, the metals
15 can be physically and intimately admixed with the zeolite using standard methods
16 known to the art.
17

18 Typical ion exchange techniques involve contacting the zeolite with a solution
19 containing a salt of the desired replacing cation or cations. Although a wide variety of
20 salts can be employed, chlorides and other halides, acetates, nitrates, and sulfates are
21 particularly preferred. The zeolite is usually calcined prior to the ion-exchange
22 procedure to remove the organic matter present in the channels and on the surface,
23 since this results in a more effective ion exchange. Representative ion exchange
24 techniques are disclosed in a wide variety of patents including U.S. Patent
25 Nos. 3,140,249 issued on July 7, 1964 to Plank, et al.; 3,140,251 issued on July 7,
26 1964 to Plank, et al.; and 3,140,253 issued on July 7, 1964 to Plank, et al.
27

28 Following contact with the salt solution of the desired replacing cation, the
29 zeolite is typically washed with water and dried at temperatures ranging from 65°C to
30 about 200°C. After washing, the zeolite can be calcined in air or inert gas at
31 temperatures ranging from about 200°C to about 800°C for periods of time ranging
32 from 1 to 48 hours, or more, to produce a catalytically active product especially useful
33 in hydrocarbon conversion processes.
34

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01 Regardless of the cations present in the synthesized form of Me-UTD-1, the
02 spatial arrangement of the atoms which form the basic crystal lattice of the zeolite
03 remains essentially unchanged.

04 Me-UTD-1 can be formed into a wide variety of physical shapes. Generally
05 speaking, the zeolite can be in the form of a powder, a granule, or a molded product,
06 such as extrudate having a particle size sufficient to pass through a 2-mesh (Tyler)
07 screen and be retained on a 400-mesh (Tyler) screen. In cases where the catalyst is
08 molded, such as by extrusion with an organic binder, the aluminosilicate can be
09 extruded before drying, or, dried or partially dried and then extruded.
10

11 Me-UTD-1 can be composited with other materials resistant to the
12 temperatures and other conditions employed in organic conversion processes. Such
13 matrix materials include active and inactive materials and synthetic or naturally
14 occurring zeolites as well as inorganic materials such as clays, silica and metal oxides.
15 Examples of such materials and the manner in which they can be used are disclosed in
16 United States Patent No. 4,910,006, issued May 20, 1990 to Zones et al., and U.S.
17 Patent No. 5,316,753, issued May 31, 1994 to Nakagawa, both of which are
18 incorporated by reference herein in their entirety.
19

20 Hydrocarbon Conversion Processes

21 Me-UTD-1 zeolites are useful in hydrocarbon conversion reactions.
22 Hydrocarbon conversion reactions are chemical and catalytic processes in which
23 carbon containing compounds are changed to different carbon containing compounds.
24 Examples of hydrocarbon conversion reactions in which Me-UTD-1 are expected to be
25 useful include catalytic cracking, hydrocracking, dewaxing, alkylation, and olefin and
26 aromatics formation reactions. The catalysts are also expected to be useful in other
27 petroleum refining and hydrocarbon conversion reactions such as isomerizing
28 n-paraffins and naphthenes, polymerizing and oligomerizing olefinic or acetylenic
29 compounds such as isobutylene and butene-1, reforming, alkylating (including the
30 alkylation of aromatics with other hydrocarbons), isomerizing polyalkyl substituted
31 aromatics (e.g., m-xylene), and disproportionating aromatics (e.g., toluene) to provide
32 mixtures of benzene, xylenes and higher methylbenzenes and oxidation reactions. Also
33 included are rearrangement reactions to make various naphthalene derivatives. The
34

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1 Me-UTD-1 catalysts have high selectivity, and under hydrocarbon conversion
2 conditions can provide a high percentage of desired products relative to total products.
3 Me-UTD-1 zeolites can be used in processing hydrocarbonaceous feedstocks.
4 Hydrocarbonaceous feedstocks contain carbon compounds and can be from many
5 different sources, such as virgin petroleum fractions, recycle petroleum fractions, shale
6 oil, liquefied coal, tar sand oil, synthetic paraffins from normal alpha olefins, recycled
7 plastic feedstocks, and, in general, can be any carbon-containing feedstock susceptible
8 to zeolitic catalytic reactions. Depending on the type of processing the
9 hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals,
10 it can also have high or low nitrogen or sulfur impurities. It can be appreciated,
11 however, that in general processing will be more efficient (and the catalyst more
12 active) the lower the metal, nitrogen, and sulfur content of the feedstock.

13 For some reactions it is preferred that the Me-UTD-1 have acid sites. For
14 those reactions, it is preferred that the Me-UTD-1 zeolite be predominantly in its
15 hydrogen ion form, i.e., it is preferred that, after calcination, at least about 80% of the
16 cation sites are occupied by hydrogen ions and/or rare earth ions.

17 The conversion of hydrocarbonaceous feeds can take place in any convenient
18 mode, for example, in fluidized bed, moving bed, or fixed bed reactors depending on
19 the types of process desired. The formulation of the catalyst particles will vary
20 depending on the conversion process and method of operation.

21 Other reactions which can be performed using the catalyst of this invention
22 containing a metal, e.g., a Group VIII metal such platinum, include
23 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization
24 reactions.

25 The following table indicates typical reaction conditions which may be
26 employed when using catalysts comprising Me-UTD-1 in the hydrocarbon conversion
27 reactions of this invention. Preferred conditions are indicated in parentheses.
28

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475	15-3000 psig	0.1-20

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Process	Temp., °C	Pressure	LHSV
	(250-450)	(200-3000)	(0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar	0.1-15
Cat. cracking	127-885	subatm. ¹ (atm.-5 atm.)	0.5-50
Oligomerization	232-649 ² 10-232 ⁴ (27-204) ⁴	0.1-50 atm. ^{2,3}	0.2-50 ² 0.05-20 ⁵ (0.1-10) ⁵
Paraffins to aromatics	100-700	0-1000 psig	0.5-40 ³
Condensation of alcohols	260-538	0.5-1000 psig	0.5-50 ³
Isomerization	93-538 (204-315)	50-1000 psig	1-10 (1-4)
Xylene isomerization	260-593 ² (315-566) ² 38-371 ⁴	0.5-50 atm. ² (1-5 atm) ² 1-200 atm. ⁴	0.1-100 ⁵ (0.5-50) ⁵ 0.5-50

1 ¹ Several hundred atmospheres2 ² Gas phase reaction3 ³ Hydrocarbon partial pressure4 ⁴ Liquid phase reaction5 ⁵ WHSV

6 Other reaction conditions and parameters are provided below.

Hydrocracking

8 Using a catalyst which comprises Me-UTD-1 in the hydrogen form and a
 9 hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and other
 10 hydrocrackate charge stocks can be hydrocracked using the process conditions and
 11 catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and
 12 U.S. Patent No. 5,316,753.

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01 The hydrocracking catalysts contain an effective amount of at least one
02 hydrogenation component of the type commonly employed in hydrocracking catalysts.
03 The hydrogenation component is generally selected from the group of hydrogenation
04 catalysts consisting of one or more metals of Group VIB and Group VIII, including
05 the salts, complexes and solutions containing such. The hydrogenation catalyst is
06 preferably selected from the group of metals, salts and complexes thereof of the group
07 consisting of at least one of platinum, palladium, rhodium, iridium, ruthenium and
08 mixtures thereof or the group consisting of at least one of nickel, molybdenum, cobalt,
09 tungsten, titanium, chromium and mixtures thereof. Reference to the catalytically
10 active metal or metals is intended to encompass such metal or metals in the elemental
11 state or in some form such as an oxide, sulfide, halide, carboxylate and the like. The
12 hydrogenation catalyst is present in an effective amount to provide the hydrogenation
13 function of the hydrocracking catalyst, and preferably in the range of from 0.05 to 25%
14 by weight.

Dewaxing

Me-UTD-1 in the hydrogen form can be used to dewax hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically, the viscosity index of the dewaxed product is improved (compared to the waxy feed) when the waxy feed is contacted with Me-UTD-1 under isomerization dewaxing conditions.

The catalytic dewaxing conditions are dependent in large measure on the feed used and upon the desired pour point. Hydrogen is preferably present in the reaction zone during the catalytic dewaxing process. The hydrogen to feed ratio is typically between about 500 and about 30,000 SCF/bbl (standard cubic feet per barrel), preferably about 1000 to about 20,000 SCF/bbl. Generally, hydrogen will be separated from the product and recycled to the reaction zone. Typical feedstocks include light gas oil, heavy gas oils and reduced crudes boiling above about 350°F. Bright stock may also be used as the feedstock.

A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil feedstock boiling above about 350°F and containing straight chain and slightly branched chain hydrocarbons by contacting the hydrocarbon oil feedstock in the

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01 presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi with a
02 catalyst comprising Me-UTD-1 and at least one group VIII metal.

03 The Me-UTD-1 hydrodewaxing catalyst may optionally contain a
04 hydrogenation component of the type commonly employed in dewaxing catalysts. See
05 the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for
06 examples of these hydrogenation components.
07

08 The hydrogenation component is present in an effective amount to provide an
09 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of
10 from about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase
11 isodewaxing at the expense of cracking reactions.
12

13 The feed may be hydrocracked, followed by dewaxing. This type of two stage
14 process and typical hydrocracking conditions are described in U.S. Patent
15 No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated herein by
16 reference in its entirety.
17

18 Me-UTD-1 may also be utilized as a dewaxing catalyst in the form of a layered
19 catalyst. That is, the catalyst comprises a first layer comprising zeolite Me-UTD-1 and
20 at least one Group VIII metal, and a second layer comprising an aluminosilicate zeolite
21 which is more shape selective than zeolite Me-UTD-1. The use of layered catalysts is
22 disclosed in U.S. Patent No. 5,149,421, issued September 22, 1992 to Miller, which is
23 incorporated by reference herein in its entirety. The layering may also include a bed of
24 Me-UTD-1 layered with a non-zeolitic component designed for either hydrocracking
25 or hydrofinishing.
26

27 Me-UTD-1 may also be used to dewax raffinates, including bright stock, under
28 conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1,
29 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.
30

31 It is often desirable to use mild hydrogenation (sometimes referred to as
32 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step
33 can be performed either before or after the dewaxing step, and preferably after.
34 Hydrofinishing is typically conducted at temperatures ranging from about 190°C to
about 340°C at pressures from about 400 psig to about 3000 psig at space velocities
(LHSV) between about 0.1 and 20 and a hydrogen recycle rate of about 400 to 1500

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01 SCF/bbl. The hydrogenation catalyst employed must be active enough not only to
02 hydrogenate the olefins, diolefins and color bodies which may be present, but also to
03 reduce the aromatic content. Suitable hydrogenation catalyst are disclosed in U. S.
04 Patent No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated by
05 reference herein in its entirety. The hydrofinishing step is beneficial in preparing an
06 acceptably stable product (e.g., a lubricating oil) since dewaxed products prepared
07 from hydrocracked stocks tend to be unstable to air and light and tend to form sludges
08 spontaneously and quickly.

10 Lube oil may be prepared using Me-UTD-1. For example, a C₂₀₊ lube oil may be
11 made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising Me-UTD-1 in the
12 hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil
13 may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous
14 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically
15 dewaxing the effluent at a temperature of at least about 400°F and at a pressure of
16 from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a
17 catalyst comprising Me-UTD-1 in the hydrogen form and at least one Group VIII
18 metal.

21 Aromatics Formation

22 Me-UTD-1 can be used to convert light straight run naphthas and similar
23 mixtures to highly aromatic mixtures. Thus, normal and slightly branched chain
24 hydrocarbons, preferably having a boiling range above about 40°C and less than about
25 200°C, can be converted to products having a substantial higher octane aromatics
26 content by contacting the hydrocarbon feed with a catalyst comprising Me-UTD-1. It
27 is also possible to convert heavier feeds into BTX or naphthalene derivatives of value
28 using the catalysts of this invention.

30 The conversion catalyst preferably contains a Group VIII metal compound to
31 have sufficient activity for commercial use. By Group VIII metal compound as used
32 herein is meant the metal itself or a compound thereof. The Group VIII noble metals
33 and their compounds, platinum, palladium, and iridium, or combinations thereof can be
34 used. Rhenium or tin or a mixture thereof may also be used in conjunction with the
Group VIII metal compound and preferably a noble metal compound. The most

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01 preferred metal is platinum. The amount of Group VIII metal present in the
02 conversion catalyst should be within the normal range of use in reforming catalysts,
03 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.
04

05 It is critical to the selective production of aromatics in useful quantities that the
06 conversion catalyst be substantially free of acidity, for example, by neutralizing the
07 zeolite with a basic metal, e.g., alkali metal, compound. Methods for rendering the
08 catalyst free of acidity are known in the art. See the aforementioned U.S. Patent
09 No. 4,910,006 and U.S. Patent No. 5,316,753 for a description of such methods.
10

11 The preferred alkali metals are sodium, potassium, and cesium. The zeolite
12 itself can be substantially free of acidity only at very high silica:alumina mole ratios.
13

Catalytic Cracking

14 Hydrocarbon cracking stocks can be catalytically cracked in the absence of
15 hydrogen using Me-UTD-1 in the hydrogen form.
16

17 When Me-UTD-1 is used as a catalytic cracking catalyst in the absence of
18 hydrogen, the catalyst may be employed in conjunction with traditional cracking
19 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking
20 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of
21 these traditional cracking catalysts are disclosed in the aforementioned U.S. Patent
22 No. 4,910,006 and U.S. Patent No 5,316,753. When a traditional cracking catalyst
23 (TC) component is employed, the relative weight ratio of the TC to the Me-UTD-1 is
24 generally between about 1:10 and about 500:1, desirably between about 1:10 and
25 about 200:1, preferably between about 1:2 and about 50:1, and most preferably is
26 between about 1:1 and about 20:1. The zeolite of this invention and/or the traditional
27 cracking catalyst may be further ion-exchanged with rare earth ions to modify
28 selectivity.
29

30 The cracking catalysts are typically employed with an inorganic oxide matrix
31 component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
32 No. 5,316,753 for examples of such matrix components.
33

Oligomerization

34 It is expected that Me-UTD-1 in the hydrogen form can also be used to
oligomerize straight and branched chain olefins having from about 2 to 21 and

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01 preferably 2-5 carbon atoms. The oligomers which are the products of the process are
02 medium to heavy olefins which are useful for both fuels, i.e., gasoline or a gasoline
03 blending stock and chemicals.

04 The oligomerization process comprises contacting the olefin feedstock in the
05 gaseous or liquid phase with a catalyst comprising Me-UTD-1.

06 The zeolite can have the original cations associated therewith replaced by a
07 wide variety of other cations according to techniques well known in the art. Typical
08 cations would include hydrogen, ammonium and metal cations including mixtures of
09 the same. Of the replacing metallic cations, particular preference is given to cations of
10 metals such as rare earth metals, manganese, calcium, as well as metals of Group II of
11 the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table, e.g., nickel. One
12 of the prime requisites is that the zeolite have a fairly low aromatization activity, i.e., in
13 which the amount of aromatics produced is not more than about 20% by weight. This
14 is accomplished by using a zeolite with controlled acid activity [alpha value] of from
15 about 0.1 to about 120, preferably from about 0.1 to about 100, as measured by its
16 ability to crack n-hexane.

17 Alpha values are defined by a standard test known in the art, e.g., as shown in
18 U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens, et al. which is
19 incorporated totally herein by reference. If required, such zeolites may be obtained by
20 steaming, by use in a conversion process or by any other method which may occur to
21 one skilled in this art.

22 Conversion of Paraffins to Aromatics

23 Me-UTD-1 in the hydrogen form can be used to convert light gas C₂-C₆
24 paraffins to higher molecular weight hydrocarbons including aromatic compounds.
25 Preferably, the zeolite will contain a catalyst metal or metal oxide wherein said metal is
26 selected from the group consisting of Group IB, IIB, VIII and IIIA of the Periodic
27 Table. Preferably the metal is gallium, niobium, indium or zinc in the range of from
28 about 0.05 to 5% by weight.

29 Condensation of Alcohols

30 Me-UTD-1 can be used to condense lower aliphatic alcohols having 1 to 10
31 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed

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01 aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent
02 No. 3,894,107 issued July 8, 1975 to Butter et al., describes the process conditions
03 used in this process, which patent is incorporated totally herein by reference.
04

05 The catalyst may be in the hydrogen form or may be base exchanged or
06 impregnated to contain ammonium or a metal cation complement, preferably in the
07 range of from about 0.05 to 5% by weight. The metal cations that may be present
08 include any of the metals of the Groups I through VIII of the Periodic Table.
09 However, in the case of Group IA metals, the cation content should in no case be so
10 large as to effectively inactivate the catalyst, nor should the exchange be such as to
11 eliminate all acidity. There may be other processes involving treatment of oxygenated
12 substrates where a basic catalyst is desired.
13

14 Isomerization

15 The present catalyst is highly active and highly selective for isomerizing C₄ to
16 C₇ hydrocarbons. The activity means that the catalyst can operate at relatively low
17 temperature which thermodynamically favors highly branched paraffins. Consequently,
18 the catalyst can produce a high octane product. The high selectivity means that a
19 relatively high liquid yield can be achieved when the catalyst is run at a high octane.
20

21 The present process comprises contacting the isomerization catalyst, i.e., a
22 catalyst comprising Me-UTD-1 in the hydrogen form, with a hydrocarbon feed under
23 isomerization conditions. The feed is preferably a light straight run fraction, boiling
24 within the range of 30°F to 250°F and preferably from 60°F to 200°F. Preferably, the
25 hydrocarbon feed for the process comprises a substantial amount of C₄ to C₇ normal
26 and slightly branched low octane hydrocarbons, more preferably C₅ and C₆
27 hydrocarbons.
28

29 It is preferable to carry out the isomerization reaction in the presence of
30 hydrogen. Preferably, hydrogen is added to give a hydrogen to hydrocarbon ratio
31 (H₂/HC) of between 0.5 and 10 H₂/HC, more preferably between 1 and 8 H₂/HC. See
32 the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a
33 further discussion of isomerization process conditions.
34

A low sulfur feed is especially preferred in the present process. The feed
preferably contains less than 10 ppm, more preferably less than 1 ppm, and most

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01 preferably less than 0.1 ppm sulfur. In the case of a feed which is not already low in
02 sulfur, acceptable levels can be reached by hydrogenating the feed in a presaturation
03 zone with a hydrogenating catalyst which is resistant to sulfur poisoning. See the
04 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a
05 further discussion of this hydrodesulfurization process.
06

07 It is preferable to limit the nitrogen level and the water content of the feed.
08 Catalysts and processes which are suitable for these purposes are known to those
09 skilled in the art.

10 After a period of operation, the catalyst can become deactivated by sulfur or
11 coke. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
12 No. 5,316,753 for a further discussion of methods of removing this sulfur and coke,
13 and of regenerating the catalyst.

14 The conversion catalyst preferably contains a Group VIII metal compound to
15 have sufficient activity for commercial use. By Group VIII metal compound as used
16 herein is meant the metal itself or a compound thereof. The Group VIII noble metals
17 and their compounds, platinum, palladium, and iridium, or combinations thereof can be
18 used. Rhenium and tin may also be used in conjunction with the noble metal. The
19 most preferred metal is platinum. The amount of Group VIII metal present in the
20 conversion catalyst should be within the normal range of use in isomerizing catalysts,
21 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.
22

Alkylation and Transalkylation

23 Me-UTD-1 can be used in a process for the alkylation or transalkylation of an
24 aromatic hydrocarbon. The process comprises contacting the aromatic hydrocarbon
25 with a C₂ to C₁₆ olefin alkylating agent or a polyalkyl aromatic hydrocarbon
26 transalkylating agent, under at least partial liquid phase conditions, and in the presence
27 of a catalyst comprising Me-UTD-1.

28 Me-UTD-1 can also be used for removing benzene from gasoline by alkylating
29 the benzene as described above and removing the alkylated product from the gasoline.

30 For high catalytic activity, the Me-UTD-1 zeolite should be predominantly in
31 its hydrogen ion form. It is preferred that, after calcination, at least about 80% of the
32 cation sites are occupied by hydrogen ions and/or rare earth ions.

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01 Examples of suitable aromatic hydrocarbon feedstocks which may be alkylated
02 or transalkylated by the process of the invention include aromatic compounds such as
03 benzene, toluene and xylene. The preferred aromatic hydrocarbon is benzene. There
04 may be occasions where naphthalene derivatives may be desirable. Mixtures of
05 aromatic hydrocarbons may also be employed.

07 Suitable olefins for the alkylation of the aromatic hydrocarbon are those
08 containing 2 to 20, preferably 2 to 4, carbon atoms, such as ethylene, propylene,
09 butene-1, trans-butene-2 and cis-butene-2, or mixtures thereof. There may be
10 instances where pentenes are desirable in this same relationship. The preferred olefins
11 are ethylene and propylene. Longer chain alpha olefins may be used as well.

13 When transalkylation is desired, the transalkylating agent is a polyalkyl
14 aromatic hydrocarbon containing two or more alkyl groups that each may have from 2
15 to about 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons
16 include di-, tri- and tetra-alkyl aromatic hydrocarbons, such as diethylbenzene,
17 triethylbenzene, diethylmethylbenzene (diethyltoluene), di-isopropylbenzene,
18 di-isopropyltoluene, dibutylbenzene, and the like. Preferred polyalkyl aromatic
19 hydrocarbons are the dialkyl benzenes. A particularly preferred polyalkyl aromatic
20 hydrocarbon is di-isopropylbenzene.

22 When alkylation is the process conducted, reaction conditions are as follows.
23 The aromatic hydrocarbon feed should be present in stoichiometric excess. It is
24 preferred that molar ratio of aromatics to olefins be greater than four-to-one to prevent
25 rapid catalyst fouling. The reaction temperature may range from 100°F to 600°F,
26 preferably 250°F to 450°F. The reaction pressure should be sufficient to maintain at
27 least a partial liquid phase in order to retard catalyst fouling. This is typically 50 psig
28 to 1000 psig depending on the feedstock and reaction temperature. Contact time may
29 range from 10 seconds to 10 hours, but is usually from 5 minutes to an hour. The
30 weight hourly space velocity (WHSV), in terms of grams (pounds) of aromatic
31 hydrocarbon and olefin per gram (pound) of catalyst per hour, is generally within the
32 range of about 0.5 to 50.

34 When transalkylation is the process conducted, the molar ratio of aromatic
hydrocarbon to polyalkyl aromatic hydrocarbon will generally range from about 1:1 to

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01 25:1, and preferably from about 2:1 to 20:1. The reaction temperature may range from
02 about 100°F to 600°F, but it is preferably about 250°F to 450°F. The reaction
03 pressure should be sufficient to maintain at least a partial liquid phase, typically in the
04 range of about 50 psig to 1000 psig, preferably 300 psig to 600 psig. The weight
05 hourly space velocity will range from about 0.1 to 10. U.S. Patent No. 5,082,990
06 issued on January 21, 1992 to Hsieh, et al. describes such processes and is
07 incorporated herein by reference.

08

09 Xylene Isomerization

10 Me-UTD-1 in the hydrogen form may also be useful in a process for
11 isomerizing one or more xylene isomers in a C₈ aromatic feed to obtain ortho-, meta-,
12 and para-xylene in a ratio approaching the equilibrium value. In particular, xylene
13 isomerization is used in conjunction with a separate process to manufacture para-
14 xylene. For example, a portion of the para-xylene in a mixed C₈ aromatics stream may
15 be recovered by crystallization and centrifugation. The mother liquor from the
16 crystallizer is then reacted under xylene isomerization conditions to restore ortho-,
17 meta- and para-xylenes to a near equilibrium ratio. At the same time, part of the
18 ethylbenzene in the mother liquor is converted to xylenes or to products which are
19 easily separated by filtration. The isomerate is blended with fresh feed and the
20 combined stream is distilled to remove heavy and light by-products. The resultant C₈
21 aromatics stream is then sent to the crystallizer to repeat the cycle.
22

23 Optionally, isomerization in the vapor phase is conducted in the presence of 3.0
24 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If hydrogen
25 is used, the catalyst should comprise about 0.1 to 2.0 wt% of a
26 hydrogenation/dehydrogenation component selected from Group VIII (of the Periodic
27 Table) metal component, especially platinum or nickel. By Group VIII metal
28 component is meant the metals and their compounds such as oxides and sulfides.

29
30
31
32
33
34 Optionally, the isomerization feed may contain 10 to 90 wt% of a diluent such
as toluene, trimethylbenzene, naphthenes or paraffins.

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01

Other Uses for Me-UTD-1

02 Me-UTD-1 can also be used as an adsorbent with high selectivities based on
03 molecular sieve behavior and also based upon preferential hydrocarbon packing within
04 the pores.
05

06 Me-UTD-1 may also be used for the catalytic reduction of the oxides of
07 nitrogen in a gas stream. Typically the gas stream also contains oxygen, often a
08 stoichiometric excess thereof. Also, the Me-UTD-1 may contain a metal or metal ions
09 within or on it which are capable of catalyzing the reduction of the nitrogen oxides.
10 Examples of such metals or metal ions include copper, cobalt and mixtures thereof.
11

12 One example of such a process for the catalytic reduction of oxides of nitrogen
13 in the presence of a zeolite is disclosed in U.S. Patent No. 4,297,328, issued
14 October 27, 1981 to Ritscher et al., which is incorporated by reference herein. There,
15 the catalytic process is the combustion of carbon monoxide and hydrocarbons and the
16 catalytic reduction of the oxides of nitrogen contained in a gas stream, such as the
17 exhaust gas from an internal combustion engine. The zeolite used is metal ion-
18 exchanged, doped or loaded sufficiently so as to provide an effective amount of
19 catalytic copper metal or copper ions within or on the zeolite. In addition, the process
20 is conducted in an excess of oxidant, e.g., oxygen.
21

22

EXAMPLES

23

24

25 The following examples demonstrate but do not limit the present invention.
26

27

Example 1

28

Preparation of Template

29 Five grams of decamethyl cobalteum hexafluorophosphate (purchased) were
30 dissolved in a warmed solution of 1200 cc ethanol and 800 cc water. This solution was
31 then run through a column of Dowex 50-X8 cation exchange resin (previously
32 washed with 60% ethanol) with the complex sticking to the resin. Next a 50/50
33 solution of 2N HCl and ethanol (total = 4,500 cc) was run over the exchange resin in
34 a column in order to elute the cobalt complex as a chloride salt. The ethanol portion
was stripped off under reduced pressure and at 70°C. The remaining acidic solution

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1 was neutralized with concentrated NaOH. This solution was concentrated down, under
2 reduced pressure and heating to 800 cc. A threefold extraction was carried out with
3 chloroform using 400 cc each time. Twenty grams of anhydrous MgSO₄ was used to
4 dry the combined extracts and the solution was stripped to dryness to yield the chloride
5 salt.

6 The recovered chloride salt was then dissolved in 10 cc water and mixed with
7 20 cc of BioRad AG-1X8 hydroxide exchange resin. The resulting mixture was stirred
8 overnight, after which the resin was filtered off. The resin was then washed with a
9 little additional water and a yellow-brown solution was collected which titrated to 0.25
10 Molar in hydroxide. Additional product was monitored as coming off resin as long as
11 the yellow color was observed in the elution collection. The color can be used as a
12 measure of extent of ion-exchange in either of the two exchange steps described.

13

14 Example 2

15 Synthesis of Borosilicate B-UTD-1

16 The synthesis of a small crystal borosilicate B-UTD-1 was carried out by
17 combining the following amounts of reagents in a Teflon liner for a Parr 125 cc
18 reactor, and heating for 5 days without stirring at 150°C. Twenty grams of a 0.21 M
19 solution of the cobalteum hydroxide template of Example 1 was mixed with 3.7 cc of
20 1.0N NaOH. Lastly, 2.20 grams of calcined boron beta zeolite was added to supply
21 both the boron and silicon to the reaction. The product crystallized as clusters of very
22 small rods, and the XRD pattern was considerably line-broadened compared to the
23 pure silica version of UTD-1. The crystallite size was estimated by TEM methods to be
24 about 500-1000 Å along the C axis. The product (which still contained the template)
25 was analyzed by X-ray diffraction and the results are tabulated in Table II below.

26 TABLE II
27 As-Synthesized B-UTD-1

2 Theta	d	Relative Intensity
5.94	14.9	26
7.46	11.8	33
12.0	7.4	25

-27-

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
14.6	6.08	28
18.1	4.90	21
19.4	4.57	30
21.2	4.19	100
22.1	4.02	43
22.5	3.95	28
24.4	3.65	19

1

A very novel and unexpected aspect of this synthesis is that the recovered reaction filtrate can then be directly reused by simply adding an additional charge of calcined boron beta zeolite. No additional base need be added and the presence of dissolved sodium borates does not seem to pose a problem for the crystallization. Of course, the filtrate must contain sufficient template for the B-UTD-1 to form, but this reuse of the filtrate allows one to maximize the use of the template. In fact, this methodology can be employed yet a third time as well. With each reaction the filtrate pH is lower, and as such it might be expected that reaction crystallization times will start to lengthen. Once the effective pH of the filtrate drops below about 9, it may not be possible to reuse it. However, using this method, a very high efficiency for using the cobaltecium template can be obtained. This is an important discovery in that the cobaltecium complex is the most expensive component in the system.

Thus, the solution remaining from the reaction described above (which still contained some of the template) was transferred to a new reactor and the same amount of B-Beta as described above was added to it. The reaction was run as described above, with the resulting product being B-JTD-1

18

Example 3

Calcination of B-UTD-1

The as-made B-UTD-1 can be calcined to remove the organic material in the pores. The material was calcined at 60°C increase per hour up to 120°C where it was held for 2 hours. The atmosphere was nitrogen with a small amount of air being bled

-28-

1 into the flow. Heating was continued at 60°C per hour up to 540°C and the heating
2 was held at this temperature for 4 hours. The calcination was then taken to 600°C over
3 2 hours and held at this temperature for another 4 hours before the sample was cooled.
4 The mass loss was typically 12-15% and a gray-green solid was obtained. The
5 calcined B-UTD-1 was analyzed by X-ray diffraction and the results are tabulated in
6 Table III below.

TABLE III
Calcined B-UTD-1

2 Theta	d	Relative Intensity
6.09	14.5	94
7.71	11.5	49
14.7	6.04	9
18.3	4.86	12
19.9	4.46	16
20.3	4.37	8
21.3	4.17	100
22.1	4.01	15
22.6	3.92	10
24.4	3.64	9
25.0	3.56	10
26.3	3.39	9
28.4	3.15	9
29.4	3.04	7
32.6	2.75	8

Example 4

Conversion of B-UTD-1 to Active Acidic Form

The task of both removing cobalt and converting the high-silica borosilicate UTD-1 to its more strongly acidic aluminosilicate form was accomplished in two sequential steps. First, the calcined product of Example 3 was refluxed in 2N HCl for 1-2 days, yielding a pink solution as cobalt was dissolved. The solid was recovered,

-29-

01 briefly washed, and then reheated to 140°C in the presence of aluminum nitrate
02 solution. The proportions to form the solution were 1: 1.1: 10 for zeolite : aluminum
03 nitrate: water. The heating was carried out in a Teflon lined reactor for 3 days. At this
04 stage the aluminosilicate had lost no crystallinity. This was also true of a sample
05 analyzed just after reflux in 2N HCl solution. The aluminosilicate UTD-1 (Al-UTD-1)
06 was now ready for use in catalytic reactions. The Al-UTD-1 (calcined) was analyzed
07 and found to have a silica to alumina mole ratio of 88. It was also analyzed by X-ray
08 diffraction and the results are tabulated in Table IV below.
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-30-

1

TABLE IV

2

Al-UTD-1

2 Theta	d	Relative Intensity
5.97	14.8	100
7.60	11.6	53
9.22	9.58	6
12.4	7.11	5
14.4	6.13	7
17.9	4.93	7
19.7	4.49	16
21.1	4.21	79
21.9	4.06	10
22.4	3.96	11
23.2	3.83	6
24.2	3.67	4
25.1	3.55	3
26.0	3.43	5
27.9	3.19	3
29.3	3.05	4
29.8	3.00	5
32.2	2.78	4
35.3	2.54	3
36.7	2.45	4
37.5	2.40	4

3

4

Example 5

5

Conversion of Methanol Using Al-UTD-1

6

Al-UTD-1 material was tested as a catalyst for the conversion of methanol to higher hydrocarbons. A Al-UTD-1 sample with only a small amount of Al in the framework was run at 400°C with methanol as feed, delivered by syringe pump, at atmospheric pressure (nitrogen carrier gas) and using a space-velocity of 1.2.

-31-

01 Products from collecting the liquid phase in a cold trap, and subsequent analysis by
02 GC/MS revealed a range of polymethylated benzenes. Considerable quantities of
03 pentamethyl and hexamethyl benzene were detected, indicating large-pore zeolite
04 behavior.
05

06

07 Example 6

08 Constraint Index Determination

09 The aluminosilicate Al-UTD-1, typical of product from Example 4, in the
10 hydrogen form and calcined in air for about four hours at about 540°C was pelleted,
11 broken and meshed (20-40). About 0.50 gram was loaded into a 3/8 inch stainless
12 steel tube with alundum on both sides of the zeolite bed. After in-situ drying to about
13 538°C, the catalyst is cooled down to about 370°C in a flow of helium. A 50/50 feed
14 of n-hexane and 3-methylpentane was introduced to run a Constraint Index test for the
15 Al-UTD-1.

16 The feed conversion was 50% for the first sampling, occurring at 10 minutes of
17 reaction. The catalysts showed gradual fouling with the conversion dropping to 30%
18 after several hours. However, the C.I. value remained constant over this period,
19 measuring at 0.2. This is also consistent with a large pore zeolite, showing no steric
20 preference for cracking the smaller, linear hexane isomer. The C₅ iso/ normal ratio was
21 near 20 and in the same area as other known large pore zeolites like Zeolite Y or SSZ-
22 24.

23

24 Example 7

25 Hydrocracking

26 The Al-UTD-1 was ion-exchanged in solution to give a palladium-containing
27 zeolite. The exchange solution was buffered with ammonium hydroxide to pH 9.5-
28 10.5. The palladium salt was the tetraamine dinitrate. The intent was to achieve 0.5
29 wt.% loading of palladium. The exchange was carried out at room temperature for 3-4
30 days and, after collection by filtration, followed by washing and drying. The resulting
31 solids were calcined up to 482°C for a period of 3 hours in air. The pelleted, broken
32

-32-

01 and meshed material was packed into a reactor and prepared for reaction with
02 hexadecane under high hydrogen pressures (1200 psi).

03 At 590°F, and without titration, the conversion was already exceeding 96%.

04 The proportion of cracking to isomerization behavior was about 2/1. The C₅₊ fraction
05 over the C₄₋ was typically greater than 10 times as much.
06

07

08 Example 8

09 Preparation of Pt/Cs/Al-UTD-1

10 A sample of cesium-neutralized Al-UTD-1 was prepared by suspending 0.67 g
11 of Al-UTD-1 (prepared as described in Example 4) in 10 g of water. 0.33 Gram of
12 CsOH solution (containing 66,450 ppm Cs) was added to 5 g water. The resulting
13 CsOH solution was added to the zeolite slurry with hand shaking, and the hand shaking
14 continued for another three minutes. The suspension was then placed on a shaker and
15 shaken at room temperature for 24 hours. The pH value of the suspension was 10.0.
16

17 The suspension was filtered without washing with water, and the resulting solid
18 was air dried at room temperature overnight. The resulting solid was calcined in air
19 with the following temperature program:

- 21 - from room temperature to 250° F at a heating rate of 1° F/minute,
22 - at 250° F for 16 hours,
23 - from 250° F to 570° F at a heating rate of 1.8° F/minute,
24 - at 570° F for 2 hours,
25 - cool down from 570° F to room temperature within 5 hours.

26 The Cs/Al-UTD-1 prepared above was further exchanged to make Pt/Cs/Al-
27 UTD-1. 0.62 Gram of the above Cs/Al-UTD-1 was suspended in 10 g of water.
28 Pt(NH₃)₄Cl₂H₂O (5.6 mg) was added to 6 g water. The resulting Pt solution was
29 added to the zeolite slurry with hand shaking, and hand shaking continued for three
30 minutes. Then the suspension was placed on a shaker and shaken at room temperature
31 for 24 hours. The pH of the suspension was measured and found to be 9.6. The
32 suspension was filtered without washing with water, and the resulting solid was air
33 dried at room temperature overnight. The resulting solid was calcined in air with the
34 following temperature program:

-33-

- 01 - from room temperature to 250° F at a heating rate of 1° F/minute,
02 - at 250° F for 16 hours,
03 - from 250° F to 570° F at a heating rate of 1.8°F/minute,
04 - at 570° F for 2 hours,
05 - cool down from 570° F to room temperature within 5 hours.
06
07 The above Pt/Cs/Al-UTD-1 was tested for lack of acidity as follows:
08 The above Pt/Cs/AL-UTD-1 was pretreated in hydrogen flow (300 ml/min.)
09 using the following temperature program:
10 - from room temperature to 400° F at a heating rate of 10° F/minute,
11 - at 400° F for 30 minutes;
12 - from 400° F to 900° F at a heating rate of 16.7°F/minute.
13 - at 900° F for 1 hour,
14 - cool down to 800° F to start the reaction for the acidity test.
15
16
17 All the reactions described below were conducted in a flow-type reactor system
18 equipped with an on-line capillary GC.
19

20 The feed used for this test was anhydrous n-octane containing 20 ppm sulfur
21 (as dimethyl disulfide). The sulfur in the feed was used to poison the Pt species loaded
22 in the zeolite. After the poisoning was completed, the catalytic activity of Pt species
23 was reduced to a very low value. It is known that acid-catalyzed cracking reaction will
24 preferably result in the formation of iso-alkanes such as iso-butane. By contrast, n-
25 alkanes such as n-butane are the main products of metal-catalyzed cracking reactions.
26 Based on this background, the acidity (if any) of the catalysts is expressed by using the
27 ratio of iso-butane to n-butane (i-Bu/n-Bu) produced at a C5 yield of 95% after Pt has
28 lost its activity. The higher the (i-Bu/n-Bu) ratio, the stronger the acidity.
29
30

31 The above Pt/Cs/Al-UTD-1 had an (i-Bu/n-Bu) ratio of 0.03, which is very low
32 and reveals the complete neutralization of acid sites by Cs species in this catalysts.

33 The reaction temperature was adjusted to 930° F to obtain a C5+ yield of 95%.
34 Other reaction parameters were: pressure = 200 psig and WHSV = 3 h⁻¹.

Through this reaction, the catalyst was also sulfided for the reforming screening
to be described below.

-34-

01

02

Example 9

03

Reforming Using Pt/Cs/Al-UTD-1

04

Immediately after the acidity test described above, the sulfided Pt/Cs/Al-UTD-1 was screened in the same reactor system for reforming. A 300° F end point naphtha was used as feed and its composition is listed below. The reactions were performed at pressure = 130 psig and WHSV = 3 per hour. The reaction temperature was varied between 930 and 980° F. Results are listed below:

10

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14

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32

wt.-%

in Feed

Yield, wt.-%

at 930° F

Yield, wt.-%

at 980° F

methane	0	0.25	0.81
ethane	0	0.37	1.74
propane	0.01	0.57	2.18
butanes	0.11	0.64	1.77
pentenes	1.20	1.42	2.18
hexanes	7.61	4.75	4.85
benzene	0.37	1.36	1.44
toluene	4.03	8.32	8.77
EB + xylenes	8.14	14.77	16.66
C9 aromatics	0.23	1.77	2.82
C7-C9 sats	74.57	3.66	2.31
unknowns	3.73	5.14	7.21
C5+ total	99.88	97.12	92.26

Example 10

33

34

The Spaciousness Index (SI) is defined as the yield ratio of iso-butane and n-butane in hydrocracking of a C10-cycloalkane such as n-butylcyclohexane over bifunctional zeolites or other molecular sieve materials. The ratio increases with increasing pore size and is, therefore, a valuable tool for characterizing the shape selective properties

-35-

01 of molecular sieve materials. Based on the results of a variation of nature and amount
02 of the noble metal exchanged into the acid zeolites, the use of Pd as hydrogenation/
03 dehydrogenation component is recommended. The optimum Pd loading is around 0.27
04 wt.%. In addition, experimental data reveal that the Spaciousness Index (SI) is under
05 certain circumstances independent of (i) the reaction temperature, (ii) the Si/Al ratio of
06 zeolite and (iii) the crystal size. Hence, it represents a characteristic constant for a
07 given zeolite.
08

09

10 There are several publications on the Spaciousness Index (SI). The main two
11 references are:
12

13

14 (i) J. Weitkamp, S. Ernst and R. Kumar, Appl. Catal. 27 (1986) 207-210.
15 (ii) J. Weitkamp, S. Ernst and C.Y. Chen, in "Zeolites: Facts, Figures, Future", pp.
16 1115 - 1129, Proceedings of the 8th International Zeolite Conference, Amsterdam,
17 The Netherlands, July 10-14, 1989, Studies in Surface Science and Catalysis, Vol.
18 49, edited by P.A. Jacobs and R.A. van Santen, Publisher: Elsevier, Amsterdam -
20 Oxford - New York - Tokyo, 1989.

21

22 For the determination of the Spaciousness Index, Pd/Al-UTD-1 (0.27 wt.% Pd) was
23 pretreated in hydrogen flow (300 ml/min.) using the following temperature program:
24
25 - from room temperature to 660° F at a heating rate of 2°F/minute,
26 - at 660° F for 10 hours,
27 - cool down to certain reaction temperature (e.g., 480° F) to start the
28 determination of the Spaciousness Index.
29

30

31 The reactions were performed at pressure = 130 psig and WHSV = 3 h⁻¹. The reaction
32 temperature was varied between 430 and 660° F. n-Butylcyclohexane was used as
33 feed.
34

Based on the results, it was determined that the Pd/Al-UTD-1 has a Spaciousness Index of 11.5, where the yield of hydrocracking products ranges between 15 and 65 %.

-36-

- 1 In the literature, the following values of the SI are reported for various zeolites: 21.0
2 (Y), 20.5 (ZSM-20), 19.0 (Beta), 17.0 (L), 12.5 (ZSM-25), 7.5 (mordenite), 5.0 (EU-
3 I and offretite), 4.0 (SAPO-5), 3.0 (ZSM-12) and 1.0 (ZSM-5/-11/-22/-23).
4 According to the above SI values, the effective pore size of the Pd/Al-UTD-1 is
5 smaller than the effective diameter of the largest voids in Y, ZSM-20, beta and L but
6 larger than those of other one-dimensional 12-membered ring zeolites.

7

8 Example 11

9 Pt- Containing All-Silica UTD-1 Constraint Index

10 A sample of all-silica UTD-1 was prepared in a manner similar to that described
11 in U. S. Patent No. 5,489,424. It was calcined and analyzed by X-ray diffraction and
12 the results are tabulated in Table V below

13 TABLE V
14 Calcined All-silica UTD-1

2 Theta	d	Relative Intensity
5.938	14.87	100
7.559	11.69	56.8
9.233	9.57	5.6
10.318	8.57	1.3
14.432	6.13	6.5
18.069	4.91	6.2
19.703	4.50	10.0
20.149	4.40	3.0
21.002	4.23	26.4
21.861	4.06	5.4
22.398	3.97	3.1
23.035	3.86	2.5
24.220	3.67	7.1
24.886	3.58	5.7
26.093	3.41	3.2
28.131	3.17	2.1

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<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
29.784	3.00	2.1
32.257	2.77	2.3

1
2 The sample was platinum exchanged in a manner similar to that described in
3 Example 7 (nominal loading of Pt 0.5 wt%) and calcined. The Constraint Index of the
4 resulting material was determined using the procedure of Example 6 at 800°F. After
5 ten minutes, the conversion was about 10%. A spectrum of aromatics was made with
6 the following ratios:

7 Benzene 2.45
8 Toluene 1.00
9 Xylenes 1.75
10 C₉ and higher 2.80
11

01 WHAT IS CLAIMED IS:

02

03 1. An aluminosilicate zeolite having a silica/alumina mole ratio of about 500 or less,
04 having pores with at least one cross-sectional dimension greater than 7.5
05 Angstroms.

06

07

08 2. A zeolite comprising a first oxide selected from the group consisting of silicon
09 oxide, germanium oxide and mixtures thereof and a second oxide selected from
10 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide
11 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
12 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
13 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
14 the second oxide of about 500 or less.

15

16

17 3. A zeolite according to Claim 2 wherein the oxides comprise silicon oxide and
18 aluminum oxide.

19

20

21 4. A zeolite according to Claim 2 wherein said zeolite is predominantly in the
22 hydrogen form.

23

24

25 5. A zeolite according to Claim 2 made substantially free of acidity by neutralizing
26 said zeolite with a basic metal.

27

28

29 6. A zeolite according to Claim 2 having a crystallite size, as estimated by TEM
30 along the C axis, of about 2000 Å or less.

31

32

33 7. A zeolite according to Claim 6 wherein the crystallite size is about 500 to 1000
34 Å.

-39-

- 01 8. A method of preparing a boron-containing zeolite comprising oxides of boron
02 and silica, said zeolite having, after calcination, the X-ray diffraction lines of
03 Table I, said method comprising:
04 (a) preparing an aqueous solution containing calcined boron-containing Beta
05 zeolite, an alkali metal or alkaline earth metal cation, and a
06 bis(pentamethylcyclopentadienyl) cobalt (III) ion having an anionic
07 counterion which is not detrimental to the formation of the boron-
08 containing zeolite;
09 (b) maintaining the aqueous solution under conditions sufficient to form
10 crystals of the boron-containing zeolite; and
11 (c) recovering crystals of the boron-containing zeolite.
12
13
14
15 9. A process for converting hydrocarbons comprising contacting a
16 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst
17 comprising a zeolite comprising a first oxide selected from the group consisting
18 of silicon oxide, germanium oxide and mixtures thereof and a second oxide
19 selected from the group consisting of aluminum oxide, gallium oxide, iron oxide,
20 indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron
21 oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having,
22 after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of
23 the first oxide to the second oxide of about 500 or less.
24
25
26
27 10. The process of Claim 9 wherein the zeolite is predominantly in the hydrogen
28 form.
29
30
31 11. The process of Claim 9 wherein the process is a hydrocracking process
32 comprising contacting a hydrocarbon feedstock under hydrocracking conditions
33 with a catalyst comprising a zeolite comprising a first oxide selected from the
34 group consisting of silicon oxide, germanium oxide and mixtures thereof and a
second oxide selected from the group consisting of aluminum oxide, gallium
oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,

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- 01 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,
02 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and
03 having a mole ratio of the first oxide to the second oxide of about 500 or less.
04
- 05
- 06 12. The process of Claim 11 wherein the zeolite is predominantly in the hydrogen
07 form.
- 08
- 09 13. The process of Claim 9 wherein the process is a dewaxing process comprising
10 contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst
11 comprising a zeolite comprising a first oxide selected from the group consisting
12 of silicon oxide, germanium oxide and mixtures thereof and a second oxide
13 selected from the group consisting of aluminum oxide, gallium oxide, iron oxide,
14 indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron
15 oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having,
16 after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of
17 the first oxide to the second oxide of about 500 or less.
18
- 19
- 20
- 21 14. The process of Claim 13 wherein the zeolite is predominantly in the hydrogen
22 form.
- 23
- 24
- 25 15. The process of Claim 9 wherein the process is a process for improving the
26 viscosity index of the dewaxed product of waxy hydrocarbon feeds comprising
27 contacting the waxy hydrocarbon feed under isomerization dewaxing conditions
28 with a catalyst comprising a zeolite comprising a first oxide selected from the
29 group consisting of silicon oxide, germanium oxide and mixtures thereof and a
30 second oxide selected from the group consisting of aluminum oxide, gallium
31 oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,
32 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,
33 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and
34 having a mole ratio of the first oxide to the second oxide of about 500 or less.

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- 01 16. The process of Claim 15 wherein the zeolite is predominantly in the hydrogen
02 form.
03
04 17. The process of Claim 9 wherein the process is a process for producing a C₂₀₊
05 lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed over a
06 catalyst comprising at least one Group VIII metal and a zeolite comprising a first
07 oxide selected from the group consisting of silicon oxide, germanium oxide and
08 mixtures thereof and a second oxide selected from the group consisting of
09 aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of
10 aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium
11 oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray
12 diffraction lines of Table I, and having a mole ratio of the first oxide to the
13 second oxide of about 500 or less.
14
15
16 18. The process of Claim 17 wherein the zeolite is predominantly in the hydrogen
17 form.
18
19 19. The process of Claim 9 wherein the process is a process for catalytically
20 dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing
21 straight chain and slightly branched chain hydrocarbons comprising contacting
22 said hydrocarbon oil feedstock in the presence of added hydrogen gas at a
23 hydrogen pressure of about 15-3000 psi with a catalyst comprising at least one
24 Group VIII metal and a zeolite comprising a first oxide selected from the group
25 consisting of silicon oxide, germanium oxide and mixtures thereof and a second
26 oxide selected from the group consisting of aluminum oxide, gallium oxide, iron
27 oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium
28 oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite
29 having, after calcination, the X-ray diffraction lines of Table I, and having a mole
30 ratio of the first oxide to the second oxide of about 500 or less.
31
32
33
34

-42-

- 01 20. The process of Claim 19 wherein the zeolite is predominantly in the hydrogen
02 form.
- 03
- 04 21. The process according to Claim 19 wherein said catalyst comprises a layered
05 catalyst comprising a first layer comprising at least one Group VIII metal and a
06 zeolite comprising a first oxide selected from the group consisting of silicon
07 oxide, germanium oxide and mixtures thereof and a second oxide selected from
08 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide
09 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
10 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
11 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
12 the second oxide of about 500 or less, and a second layer comprising an
13 aluminosilicate zeolite which is more shape selective than the zeolite of said first
14 layer.
- 15
- 16
- 17
- 18 22. The process of Claim 9 wherein the process is a process for preparing a
19 lubricating oil which comprises:
- 20
- 21
- 22 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain
23 an effluent comprising a hydrocracked oil; and
- 24
- 25
- 26 catalytically dewaxing said effluent comprising hydrocracked oil at a temperature
27 of at least about 400°F and at a pressure of from about 15 psig to about 3000
28 psig in the presence of added hydrogen gas with a catalyst comprising at least
29 one Group VIII metal and a zeolite comprising a first oxide selected from the
30 group consisting of silicon oxide, germanium oxide and mixtures thereof and a
31 second oxide selected from the group consisting of aluminum oxide, gallium
32 oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,
33 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,
34 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and
 having a mole ratio of the first oxide to the second oxide of about 500 or less.

- 01
- 02 23. The process of Claim 22 wherein the zeolite is predominantly in the hydrogen
- 03 form.
- 04
- 05
- 06 24. The process of Claim 9 wherein the process is a process for isomerization
- 07 dewaxing a raffinate comprising contacting said raffinate in the presence of
- 08 added hydrogen with a catalyst comprising at least one Group VIII metal and a
- 09 zeolite comprising a first oxide selected from the group consisting of silicon
- 10 oxide, germanium oxide and mixtures thereof and a second oxide selected from
- 11 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide
- 12 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
- 13 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
- 14 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
- 15 the second oxide of about 500 or less.
- 16
- 17
- 18
- 19 25. The process of Claim 24 wherein the zeolite is predominantly in the hydrogen
- 20 form.
- 21
- 22
- 23 26. The process of Claim 24 wherein the raffinate is bright stock.
- 24
- 25
- 26 27. The process of Claim 9 wherein the process is a process for increasing the octane
- 27 of a hydrocarbon feedstock to produce a product having an increased aromatics
- 28 content comprising contacting a hydrocarbonaceous feedstock which comprises
- 29 normal and slightly branched hydrocarbons having a boiling range above about
- 30 40°C and less than about 200°C, under aromatic conversion conditions with a
- 31 catalyst comprising a zeolite comprising a first oxide selected from the group
- 32 consisting of silicon oxide, germanium oxide and mixtures thereof and a second
- 33 oxide selected from the group consisting of aluminum oxide, gallium oxide, iron
- 34 oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium
- oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite

- 01 having, after calcination, the X-ray diffraction lines of Table I, and having a mole
02 ratio of the first oxide to the second oxide of about 500 or less.
- 03
- 04 28. The process of Claim 27 wherein the zeolite is substantially free of acidity.
- 05
- 06 29. The process of Claim 27 wherein the zeolite contains a Group VIII metal
07 component.
- 08
- 09
- 10 30. The process of Claim 9 wherein the process is a catalytic cracking process
11 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic
12 cracking conditions in the absence of added hydrogen with a catalyst comprising
13 a zeolite comprising a first oxide selected from the group consisting of silicon
14 oxide, germanium oxide and mixtures thereof and a second oxide selected from
15 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide
16 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
17 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
18 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
19 the second oxide of about 500 or less.
- 20
- 21
- 22
- 23 31. The process of Claim 30 wherein the zeolite is predominantly in the hydrogen
24 form.
- 25
- 26
- 27 32. The process of Claim 30 wherein the catalyst additionally comprises a large pore
28 crystalline cracking component.
- 29
- 30
- 31 33. The process of Claim 9 wherein the process is an isomerization process for
32 isomerizing C₄ to C₇ hydrocarbons, comprising contacting a catalyst, comprising
33 at least one Group VIII metal impregnated on a zeolite comprising a first oxide
34 selected from the group consisting of silicon oxide, germanium oxide and
mixtures thereof and a second oxide selected from the group consisting of
aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of

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- 01 aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium
02 oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray
03 diffraction lines of Table I, and having a mole ratio of the first oxide to the
04 second oxide of about 500 or less, with a feed having normal and slightly
05 branched C₄ to C₇ hydrocarbons under isomerizing conditions.
- 06
- 07
- 08 34. The process of Claim 33 wherein the zeolite is predominantly in the hydrogen
09 form.
- 10
- 11 35. The process of Claim 33 wherein the catalyst has been calcined in a steam/air
12 mixture at an elevated temperature after impregnation of the Group VIII metal.
- 13
- 14
- 15 36. The process of Claim 33 wherein the Group VIII metal is platinum.
- 16
- 17 37. The process of Claim 9 wherein the process is a process for alkylating an
18 aromatic hydrocarbon which comprises contacting under alkylation conditions at
19 least a mole excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at
20 least partial liquid phase conditions and in the presence of a catalyst comprising a
21 zeolite comprising a first oxide selected from the group consisting of silicon
22 oxide, germanium oxide and mixtures thereof and a second oxide selected from
23 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide
24 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
25 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
26 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
27 the second oxide of about 500 or less.
- 28
- 29
- 30
- 31
- 32 38. The process of Claim 37 wherein the olefin is a C₂ to C₄ olefin.
- 33
- 34 39. The process of Claim 37 wherein the aromatic hydrocarbon and olefin are
 present in a molar ratio of about 4:1 to about 20:1, respectively.

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- 01 40. The process of Claim 37 wherein the aromatic hydrocarbon is selected from the
02 group consisting of benzene, toluene, xylene, or mixtures thereof.
- 03
- 04 41. The process of Claim 37 wherein the zeolite is predominantly in the hydrogen
05 form.
- 06
- 07
- 08 42. The process of Claim 9 wherein the process is a process for transalkylating an
09 aromatic hydrocarbon which comprises contacting under transalkylating
10 conditions an aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon
11 under at least partial liquid phase conditions and in the presence of a catalyst
12 comprising a zeolite comprising a first oxide selected from the group consisting
13 of silicon oxide, germanium oxide and mixtures thereof and a second oxide
14 selected from the group consisting of aluminum oxide, gallium oxide, iron oxide,
15 indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron
16 oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having,
17 after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of
18 the first oxide to the second oxide of about 500 or less.
- 19
- 20
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- 22 43. The process of Claim 42 wherein the aromatic hydrocarbon and the polyalkyl
23 aromatic hydrocarbon are present in a molar ratio of from about 1:1 to about
24 25:1, respectively.
- 25
- 26
- 27 44. The process of Claim 42 wherein the aromatic hydrocarbon is a member selected
28 from the group consisting of benzene, toluene, xylene, or mixtures thereof.
- 29
- 30
- 31 45. The process of Claim 42 wherein the polyalkyl aromatic hydrocarbon is a
32 dialkylbenzene.
- 33
- 34 46. The process of Claim 42 wherein the zeolite is predominantly in the hydrogen
form.

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- 01 47. The process of Claim 9 wherein the process is a process to convert paraffins to
02 aromatics which comprises contacting paraffins with a catalyst comprising
03 gallium, zinc, or a compound of gallium or zinc and a zeolite comprising a first
04 oxide selected from the group consisting of silicon oxide, germanium oxide and
05 mixtures thereof and a second oxide selected from the group consisting of
06 aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of
07 aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium
08 oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray
09 diffraction lines of Table I, and having a mole ratio of the first oxide to the
10 second oxide of about 500 or less.
- 11
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- 14 48. The process according to Claim 47 wherein the zeolite is substantially free of
15 acidity.
- 16
- 17
- 18 49. The process of Claim 9 wherein the process is a process for isomerizing olefins
19 comprising contacting said olefin under conditions which cause isomerization of
20 the olefin with a catalyst comprising a zeolite comprising a first oxide selected
21 from the group consisting of silicon oxide, germanium oxide and mixtures
22 thereof and a second oxide selected from the group consisting of aluminum
23 oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide,
24 boron oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and
25 vanadium oxide, said zeolite having, after calcination, the X-ray diffraction lines
26 of Table I, and having a mole ratio of the first oxide to the second oxide of about
27 500 or less.
- 28
- 29
- 30
- 31 50. The process according to Claim 49 wherein the zeolite is predominantly in the
32 hydrogen form.
- 33
- 34 51. The process of Claim 9 wherein the process is a process for isomerizing an
isomerization feed comprising an aromatic C₈ stream of xylene isomers or
mixtures of xylene isomers and ethylbenzene, wherein a more nearly equilibrium

- 01 ratio of ortho-, meta and para-xylenes is obtained, said process comprising
02 contacting said feed under isomerization conditions with a catalyst comprising a
03 zeolite comprising a first oxide selected from the group consisting of silicon
04 oxide, germanium oxide and mixtures thereof and a second oxide selected from
05 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide
06 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
07 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
08 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
09 the second oxide of about 500 or less.
10
11
12 52. The process of Claim 51 wherein the zeolite is predominantly in the hydrogen
13 form.
14
15
16 53. The process of Claim 9 wherein the process is a process for oligomerizing olefins
17 comprising contacting an olefin feed under oligomerization conditions with a
18 catalyst comprising a zeolite comprising a first oxide selected from the group
19 consisting of silicon oxide, germanium oxide and mixtures thereof and a second
20 oxide selected from the group consisting of aluminum oxide, gallium oxide, iron
21 oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium
22 oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite
23 having, after calcination, the X-ray diffraction lines of Table I, and having a mole
24 ratio of the first oxide to the second oxide of about 500 or less.
25
26
27
28 54. The process of Claim 53 wherein the zeolite is predominantly in the hydrogen
29 form.
30
31
32 55. A process for converting lower alcohols and other oxygenated hydrocarbons
33 comprising contacting said lower alcohol or other oxygenated hydrocarbon
34 under conditions to produce liquid products with a catalyst comprising a zeolite
 comprising a first oxide selected from the group consisting of silicon oxide,
 germanium oxide and mixtures thereof and a second oxide selected from the

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- 01 group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and
02 mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
03 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
04 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
05 the second oxide of about 500 or less.
- 06
- 07
- 08 56. The process according to Claim 55 wherein the zeolite is predominantly in the
09 hydrogen form.
- 10
- 11 57. In a process for the reduction of oxides of nitrogen contained in a gas stream in
12 the presence of oxygen wherein said process comprises contacting the gas
13 stream with a zeolite, the improvement comprising using as the zeolite a zeolite
14 comprising a first oxide selected from the group consisting of silicon oxide,
15 germanium oxide and mixtures thereof and a second oxide selected from the
16 group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and
17 mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium
18 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,
19 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to
20 the second oxide of about 500 or less.
- 21
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- 24 58. The process of Claim 57 wherein said zeolite contains a metal or metal ions
25 capable of catalyzing the reduction of the oxides of nitrogen.
- 26
- 27
- 28 59. The process of Claim 58 wherein the metal is copper, cobalt or mixtures thereof.
- 29
- 30 60. The process of Claim 58 wherein the gas stream is the exhaust stream of an
31 internal combustion engine.
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- 34 61. A process for converting hydrocarbons comprising contacting a
 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst

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01 comprising a Group VIII metal and a silica zeolite having, after calcination, the
02 X-ray diffraction lines of Table IA.
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